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Dinuclear Systems in the Efficient Nickel-Catalyzed Kumada–Tamao–Corriu Cross-Coupling of Aryl Halides

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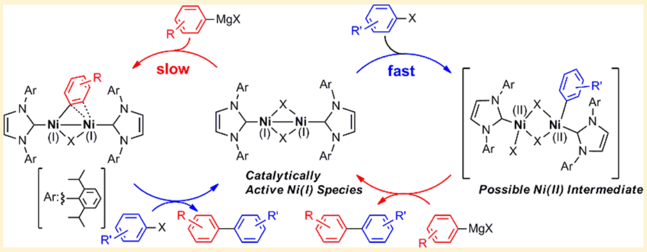
Supporting Information

ABSTRACT: Highly active dinuclear nickel(I) complexes bearing bulky N-heterocyclic carbene ligands have been shown to be involved in the catalytic cycle of the Kumada–Tamao–Corriu cross-coupling reaction of aryl halides. The results of several stoichiometric reactions and kinetics experiments have revealed that monovalent and divalent dinickel species are the active species in the highly efficient, nickel-catalyzed, Kumada coupling reactions of aryl halides.

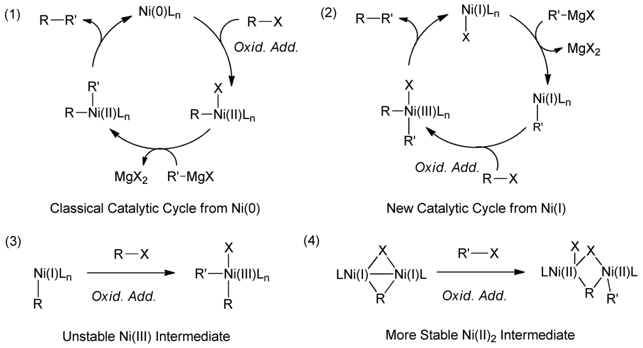


INTRODUCTION

Considerable progress has been made during the course of the last three decades toward the development of organotransition-metal-catalyzed cross-coupling reactions of aryl halides, using various metal catalysts or catalyst precursors with ligands and/or cocatalysts. These methods have been successfully applied to the synthesis of a large number of organic products for electronic devices, liquid crystals, and medicinal chemistry.[1] The Kumada–Tamao–Corriu cross-coupling reaction of an aryl or alkyl halide with a Grignard reagent in the presence of a Ni, Pd, Co, or Fe catalyst is one of the most useful reactions for the formation of aryl–aryl or alkyl–aryl bonds under mild conditions.[1]

A general catalytic system using a mixture of Ni(cod)$_2$ and a bulky N-heterocyclic carbene (NHC) ligand, such as IPr or IMes, is widely employed in various cross-coupling reactions including the Kumada–Tamao–Corriu cross-coupling reactions.[2] Despite the wide variety of substrates and applications that have been developed for coupling reactions involving Grignard reagents, very little is currently known about the mechanisms of these reactions. The classical catalytic cycle proposed for these transformations is shown in Scheme 1(1).[3] In contrast, the results of several studies involving Ni and Pd catalysts have provided evidence that radical pathways, including single-electron-transfer processes, are involved in the cross-coupling reactions.[4] We have developed a well-defined nickel(I) compound bearing a bulky NHC, NiCl(IPr)$_2$ (where IPr is 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene), which was active in the Kumada coupling reaction of aryl halides.[5] The active nickel(I) species could be generated in situ in the cross-coupling reactions reported above, because this nickel(I) complex, NiCl(IPr)$_2$, can be formed from a mixture of Ni(cod)$_2$, IPr, and an aryl halide.[5] Several other well-defined monovalent nickel complexes have also been reported to act in a range of other catalytic cycles.[6] Scheme 1(2) shows a proposed catalytic cycle between Ni(I) and Ni(III) species. It is noteworthy, however, that there have been no studies in the literature providing clear evidence of how these reactions proceed, including, for example, reports pertaining to the structures of possible intermediates. This lack of information prompted us to investigate the mechanism of the Kumada coupling reaction using monovalent nickel species to develop a deeper mechanistic understanding of the reaction. The work in

Scheme 1. (1) Classical Catalytic Cycle between Ni(0) and Ni(II), (2) Proposed Cycle between Ni(I) and Ni(III), (3) Oxidation States in the Oxidative Addition to a Monomeric Ni(I) Center, and (4) Oxidation States of the Dimeric Ni Centers



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this study is based on the hypothesis that a dinuclear nickel(I) species would be more plausible as an intermediate in these reactions than a mononuclear nickel(I) species (Scheme 1(3), (4)). This hypothesis was formed on the basis that the unpaired electrons on the nickel centers could readily form metal−metal bonds in the presence of an appropriately bulky ligand, which could stabilize the formation of coordinatively unsaturated dinuclear compounds that would be capable of performing as highly active and efficient cooperative catalysts.

Dinuclear complexes containing two linked metal atoms have attracted considerable attention as potential catalysts for a variety of organic transformations, because synergistic and cooperative effects by the multinuclei centers in catalysis can activate inert and/or specific bonds much more efficiently than the corresponding mononuclear catalysts.[7−9] However, there are very few examples in the literature of dinuclear catalysts that have been designed and applied to cross-coupling reactions. A dinuclear nickel catalyst using a multidentate ligand was used to catalyze the Negishi cross-coupling reaction of an aryl chloride, where it performed much more effectively than a mononickel catalyst system.[10] In palladium chemistry, dinuclear Pd(I) complexes have been reported to catalyze the Buchwald−Hartwig amination of aryl halides, even at room temperature.[11a] Schoenebeck et al. also recently studied catalytic cross-coupling reactions of aryl halides and the mechanism using dinuclear Pd(I) complexes.[11b−d]

With regard to the dinuclear nickel(I) complexes discussed in this report, the oxidation states of the nickel atoms could be regarded as the most important feature of their catalytic cycle. Oxidative addition to a mononuclear nickel(I) complex would lead to a formal change in oxidation state of the nickel atom from +1 to +3 (Scheme 1(3)).[3] In contrast, oxidative addition to a dinuclear nickel(I) complex would lead to a change in the formal oxidation states of both nickel atoms from +1 to +2. Therefore, we hypothesized that the two stable nickel(II) centers are generated favorably in this dinickel(I) catalyst system (Scheme 1(4)).

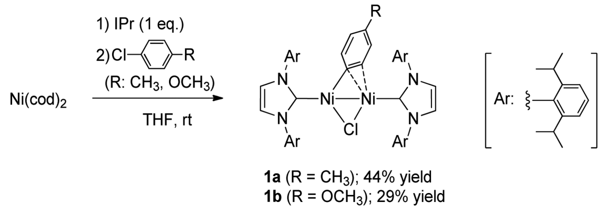
NHC ligands are some of the most versatile and useful candidates for the construction of active catalysts, because they are strongly electron donating (i.e., two electrons) and can also generate strong trans effects.[12] Bulky NHC ligands, such as IPr and IMes (where IMes is 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene), have been used to good effect in various catalytic cross-coupling reactions, providing high levels of efficiency and chemoselectivity. Among the many Ni(I) complexes reported to date bearing a range of phosphorus and other ligands,[13] several recent reports have revealed that bulky NHC ligands can also kinetically stabilize monovalent nickel species and that the resulting systems can be used to catalyze various reactions, including Kumada−Tamao−Corriu coupling,[4,6b,c] Suzuki coupling,[6a] Buchwald−Hartwig amination,[6b] and hydrodehalogenation reactions.[6d] It is noteworthy that mononuclear Ni(I) NHC complexes were used in all of these examples. On the other hand, the synthesis and stoichiometric reactions of a variety of dinuclear nickel(I) IPr complexes having a Ni−Ni single bond have been reported.[14] Taken together, these results provide a strong indication that the efficiency of catalytic reactions using these ligands would differ considerably from those using smaller ligands, most probably because of differences in the mechanisms of these reactions resulting from differences in the oxidation states of the metal centers.

Herrmann et al. reported that the catalytic activity of an in situ generated active nickel species in the Kumada−Tamao−Corriu cross-coupling of aryl fluoride was strongly dependent upon the amount of IPr added to the system.[15] The addition of 1 equiv of NHC to a nickel precursor provided a nickel species bearing one NHC ligand that was much more active than the corresponding nickel species bearing two NHC ligands generated by the addition of 2 equiv of NHC. As noted above, $NiCl(IPr)_2$ can act as an active catalyst but has two molecules of IPr.[4] Therefore, it remains unclear how a nickel catalyst bearing only one IPr ligand was more active in the cross-coupling reactions. The results of our most recent study showed that the complex formed from mixed IPr/PPh_3 and nickel(I) exhibited higher activity in the Kumada coupling reaction of aryl halides than $NiCl(IPr)_2$.[6b] Here, we found that the oxidative addition of aryl chloride to an in situ generated nickel(0) complex bearing an IPr ligand gave a coordinatively unsaturated dinuclear nickel(I) complex, which exhibited catalytic performance higher than that of the monomeric nickel(I) catalyst $NiCl(IPr)_2$. We wish to report the isolation and structural elucidation of these dinickel complexes, as well as an evaluation of their catalytic performance. The results of mechanistic studies, including stoichiometric reactions, kinetic experiments, and DFT calculations, will also be discussed.

RESULTS AND DISCUSSION

Synthesis and Structures of the Dinickel(I) Aryl Complexes. The dinuclear nickel(I) oxidative addition products $[Ni(IPr)]_2(\mu\text{-Cl})(\mu\text{-}\eta^2\text{-}C_6H_4R)$ (**1a**, R = 4-CH_3; **1b**, R = 4-OCH_3) were successfully prepared by addition of *p*-chlorotoluene and *p*-chloroanisole to a solution of $Ni(cod)_2$ and IPr (1 equiv with respect to nickel) in THF at room temperature (Scheme 2). Instead of forming the expected mononickel(II) adducts via the oxidative addition of the aryl halides to a Ni(0) center, these two oxidative addition reactions rather unexpectedly afforded **1a,b** in a selective manner. The isolated yields of **1a,b** following their purification upon recrystallization were 44 and 29%, respectively. Trace amounts of the dinuclear μ-chloride $[Ni(IPr)]_2(\mu\text{-Cl})_2$ (**2**)[16] and 4,4′-dimethylbiphenyl or 4,4′-dimethoxybiphenyl were detected in the crude ^1H NMR spectra. Addition of only IPr to a solution of $Ni(cod)_2$ in THF gave a dark green solution, which most likely contained an $(IPr)Ni^0$ THF complex rather than a $(NHC)Ni^0$ dimer (reddish brown).[17] The solution became dark reddish brown following the addition of *p*-chlorotoluene, indicating formation of the compound **1a**. In the absence of IPr, $Ni(cod)_2$ did not react with *p*-chlorotoluene under these conditions. Furthermore, the use of other nonpolar solvents, including *n*-hexane and benzene-d_6, resulted in the formation of numerous byproducts, and the addition of 2 equiv of IPr to

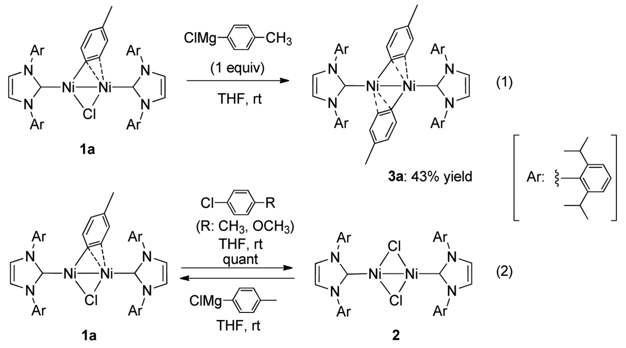
Scheme 2. Synthesis of Dinickel(I) Oxidative Addition Products 1a,b



$Ni(cod)_2$ followed by *p*-chlorotoluene resulted in the formation of the mononuclear nickel(I) product $NiCl(IPr)_2$ (**4**).[4]

Addition of 1 equiv of a Grignard reagent and aryl halide independently to compound **1a** in THF at room temperature afforded dinickel(I) complexes, representing interesting transformations. The reaction of **1a** with *p*-tolylmagnesium chloride for 18 h led to a transmetalation reaction at the bridging chloride ligand, which yielded the corresponding biaryl complex $[Ni(IPr)]_2(\sigma{:}\eta^2\text{-}C_6H_4CH_3)_2$ (**3a**) (Scheme 3(1)). The yield of **3a** as dark green crystals following its purification upon recrystallization from THF at −30 °C was 43%.

Scheme 3. Reactions of 1a (1) with Tolylmagnesium Chloride and (2) with 4-Chlorotoluene and 4-Chloroanisole and the Reverse Reaction



On the other hand, the reaction of **1a** with 4-chlorotoluene afforded the dinickel *μ*-chloride **2** (Scheme 3(2)). A similar outcome was also observed for the reaction of **1a** with several other aryl halides, including *p*-chloroanisole and chlorobenzene. The formation of **2** from the reactions of **1a** with a range of aryl halides suggested that the oxidative addition of the aryl chlorides to **1a** and the subsequent reductive elimination of the biaryl products were occurring at the unsaturated dinickel centers. Detailed experimental results and discussion are given below. Interestingly, the reverse reaction from **2** to **1a** was demonstrated by the reaction of **2** with 1.0 equiv of *p*-tolylmagnesium chloride (Scheme 3(2)). A crude ^1H NMR spectrum of the reaction showed that **1a** was being formed as the major species, together with only small amounts of **3a** and **2**. It is noteworthy that the dinuclear framework in **1a** remained intact even after the stoichiometric reactions.

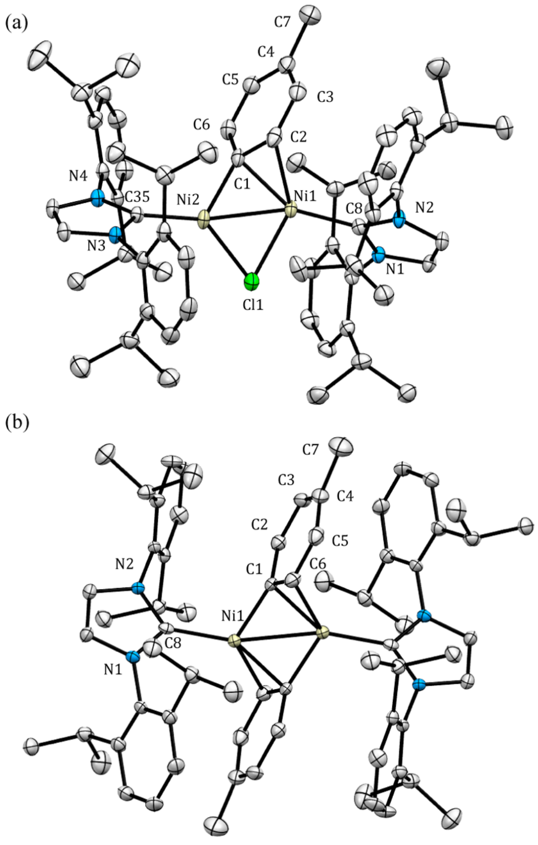


Figure 1. ORTEP drawings of (a) **1a** and (b) **3a** (thermal ellipsoids at the 50% probability level). All of the hydrogen atoms have been omitted for clarity. Half of the **3a** molecule has been shown by a symmetric operation.

The ^1H NMR spectra of **1a**,**b** showed characteristic diamagnetic high-field signals at δ 6.07 (4H in **1a**) or δ 6.17 and 6.72 (2H + 2H in **1b**), which were attributed to the aryl protons of the bridging tolyl or anisyl group. These signals indicated the occurrence of a shielding effect derived from the aryl rings of the IPr ligands, where the bridging aryl protons were located in close proximity to the aryl rings of IPr. The integrated ratio of the signals assigned as the methyl protons of the σ-tolyl or anisyl moiety and the isopropyl methine protons of the carbene ligand was 3:8, which indicated that the ratio of the σ-aryl moiety and the carbene ligand was 2:1. This observation suggested formation of an oxidative addition product bearing two NHC ligands in a manner similar to that reported by Radius et al.[18,19] for a series of nickel biscarbene complexes. However, the actual structures of **1a**,**b**, which were determined by X-ray crystallography using single crystals derived from hexane solutions, revealed, rather unexpectedly, that compounds **1a**,**b** were coordinatively unsaturated 30e dinickel adducts. The oxidation state of each nickel atom was found to be +1, and therefore in contrast to that of the divalent mononickel analogues generated as a result of the oxidative addition of aryl halides to Ni(0) complexes.[20] The distance between the two nickel centers in **1a** was found to be 2.3954(5) Å (Figure 1), which suggested the existence of a single bond.[14] One of the C=C bonds in the σ-aryl moiety was coordinated to one of the two metal centers in the η^2 mode, and the ring structure was close to that of a cyclohexatriene, in that the C3−C4 and C5−C6 bond lengths were 1.382(5) and 1.375(4) Å, shorter than the C2−C3, C4−C5, and C6−C1 bond lengths, which were 1.417(4), 1.406(4), and 1.431(4) Å, respectively. The C1−C2 bond length was elongated to 1.423(4) Å because it was π-coordinated to the nickel atom. However, solution-phase NMR analyses of compound **1a** suggested that the protons and carbons belonging to this aryl moiety, as well as those of the IPr ligand, were symmetrical.[21] The links between the two nickel atoms and the carbene carbon atoms were slightly bent, as shown by the Ni2−Ni1−C8(carbene) and Ni1−Ni2−C35(carbene) bond angles, which were 158.50(8) and 167.98(8)°, respectively. The generation of a space-filling model of **1a** from the crystal structure data revealed that the phenyl rings and the methyl groups of the two IPr ligands formed a pocket over the two nickel atoms and tightly surrounded the σ-tolyl moiety (Figure 2). The bending of the Ni−Ni−C(carbene) bond angles could therefore be explained in terms of the steric hindrance between the IPr and the tolyl groups. Depending on the leaning

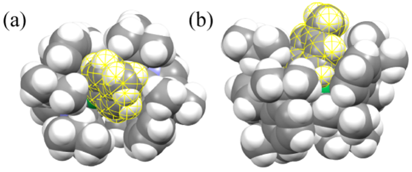


Figure 2. Space-filling models of **1a** generated from the crystallographic data (yellow mesh, σ-tolyl group; gray, carbon; white, hydrogen; green, nickel): (a) top view; (b) side view.

direction of the σ-aryl moiety in the fluxional motion in solution, the geometry of each nickel center could change slightly, which would result in a change in the Ni–Ni–C(carbene) bond angle. The crystal structure of **1b** was also determined and was found to be quite similar to that of **1a** (see the Supporting Information).

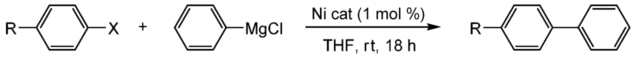
A single-crystal X-ray diffraction study of **3a** was also conducted and revealed successful incorporation of the bridging 4-tolyl group instead of chlorine. The structural features of **3a** were also found to be similar to those of **1a**, as shown in Figure 1b. The Ni–Ni distance was determined to be 2.4067(8) Å (Table 1), which indicated the presence of a bonding interaction between the two nickel atoms, and one of the C=C bonds of each σ-aryl group was coordinated to a nickel center, being similar to that observed in **1a**. Other bimetallic coordination effects for μ-σ-aryl groups have been reported in gold complexes.[22] Johnson et al. reported coordination in dinickel(I) complexes similar to that in complexes **1** and **3**.[23]

Table 1. Representative Bond Distances (Å) and Angles (deg) of 1a and 3a

1a		3a	
	Bond Distances (Å)		
Ni1–Ni2	2.3954(5)	Ni1–Ni1′	2.4067(8)
Ni1–C1	1.983(3)	Ni1–C1	1.936(3)
Ni2–C1	1.914(3)	Ni1–C6	2.376(3)
Ni1–C2	2.210(3)	Ni1–C8	1.894(3)
Ni1–C8	1.910(3)	C1–C2	1.432(4)
Ni2–C35	1.855(3)	C2–C3	1.390(4)
C1–C2	1.423(4)	C3–C4	1.395(5)
C2–C3	1.417(4)	C4–C5	1.381(5)
C3–C4	1.382(5)	C5–C6	1.415(5)
C4–C5	1.406(4)	C6–C1	1.404(4)
C5–C6	1.375(4)		
C6–C1	1.431(4)		
	Bond Angles (deg)		
Ni2–Ni1–C8	158.50(8)	Ni1′–Ni1–C8	160.12(9)
Ni1–Ni2–C35	167.98(8)	Ni1–C1–Ni1′	76.3(1)
Ni1–Cl1–Ni2	65.29(2)		
Ni1–C1–Ni2	75.8(1)		

Catalytic Application of 1a for the Kumada Coupling. Compound **1** was found to catalyze the Kumada cross-coupling reaction of weakly active aryl halides. Compounds **1a** and **4** exhibited clear differences in their catalytic activity, as shown in Table 2. For example, the coupling of 4-chloroanisole with phenylmagnesium chloride in the presence of **1a** for 18 h at ambient temperature gave 4-methoxybiphenyl in 85% yield (Table 2, entry 1). In contrast, the use of compound **4** as a catalyst resulted in a much lower yield of the cross-coupling product of 33% (Table 2, entry 3). Compound **1a** also exhibited moderate activity toward the inactive substrate 4-fluoroanisole and gave a 42% yield of the corresponding biaryl product following purification by silica gel column chromatography (Table 2, entry 2). It is noteworthy that the Kumada coupling of anisole derivatives can also yield unwanted byproducts as a result of the elimination of the methoxy group.[24] Free IPr (5 equiv relative to **4**) was added to the reaction mixture to avoid the formation of the dinickel(I) complex **2** in solution as a result of the slow equilibrium reaction between **4** and **2**. Furthermore, the rapid Kumada coupling of aryl chlorides in the presence of **2** was briefly discussed in our previous report.[6b]

Table 2. Kumada Cross-Coupling of Aryl Halides Mediated by Ni(I) Complexes

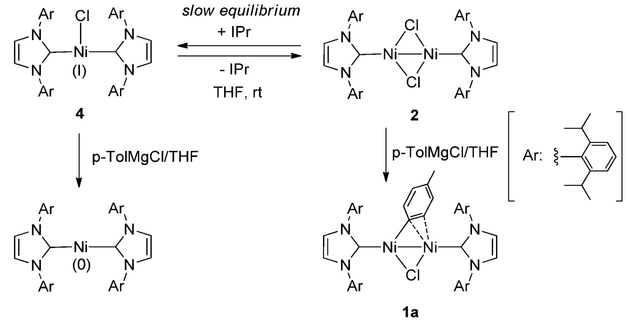


entry	cat.	R	X	additive	yield (%)[a]
1	1a	OMe	Cl		85
2	1a	OMe	F		42
3	4	OMe	Cl	IPr (5 mol %)	33
4	4	OMe	Br	IPr (5 mol %)	93
5	4	Ph	Br	IPr (5 mol %)	89

[a] Yields were determined after silica gel column chromatography as an average of at least two runs.

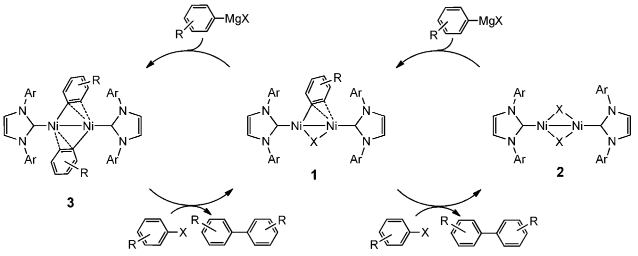
The above profiles of the Kumada coupling reactions are in good agreement with those in the literature using nickel precatalysts and the imidazolium salt IPr/HCl.[15] In our preliminary study, stoichiometric reaction of p-tolylmagnesium chloride in THF with the monomeric Ni(I) complex **4** gave not the transmetalated Ni(I) complex [$(IPr)_2NiPh$] or the dinickel(I) complex **1a** but the reduced Ni(0) compound [$(IPr)_2Ni$] (Scheme 4). It can be noted that the added amount of IPr strongly affects the catalytic processes in the Kumada cross-coupling reactions.

Scheme 4. Preliminary Stoichiometric Reactions of 2 and 4 with Phenylmagnesium Chloride



Possible Dinickel Cycles in the Kumada Coupling Reaction. The results presented above on the reactivity of the dinickel(I) species suggested the possibility of two catalytic cycles in the Kumada cross-coupling of aryl halides involving the dinickel species **1**–**3**, as shown in Scheme 5. One of these cycles would involve the reaction of compounds **1** and **2**. Briefly, the oxidative addition of an aryl halide to **1** would result in the formation of a metastable dinickel(II) species, which would smoothly eliminate the corresponding biaryl product to give **2**. Compound **1** would then be regenerated via a transmetalation reaction with arylmagnesium chloride. A similar

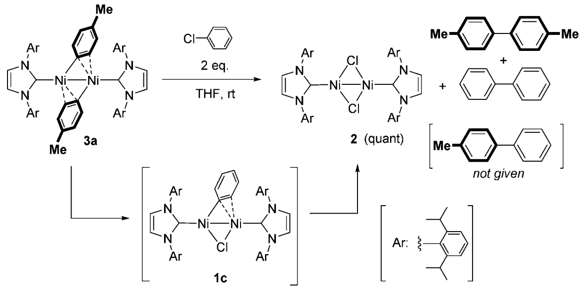
Scheme 5. Two Possible Reaction Mechanisms in the Kumada Coupling of Aryl Halides



process involving **3** as an intermediate could also be possible. In this case, the reaction of a Grignard reagent with **1** instead of an aryl halide would result in the formation of complex **3** via a transmetalation process. The reductive elimination of biaryls in the presence of an aryl halide would then form **1** as the oxidative addition product (Scheme 5).

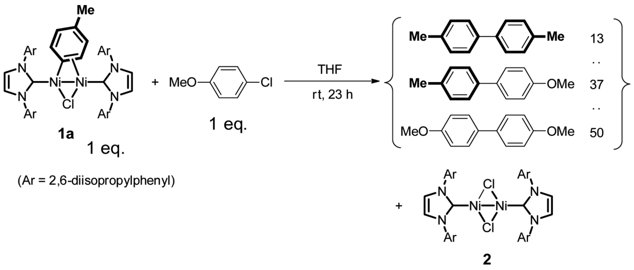
Several experiments were conducted to verify the possibility of the proposed cycles. The first of these experiments involved the reaction of **3a** with 2 equiv of chlorobenzene in THF at room temperature for 21 h. Notably, the major product of this reaction was not compound **1** but **2** (Scheme 6). It is possible that compound **1** is generated from **3** and the subsequent reaction of **1** with chlorobenzene readily occurs to yield **2** in this reaction. In addition, only 4,4′-dimethylbiphenyl and biphenyl were observed as the organic products, and no 4-methylbiphenyl was detected by GC-MS (Scheme 6). We could not detect **1c** in this reaction even when a smaller amount of chlorobenzene was added to **3**. Given that compound **3** was found to be stable in the absence of chlorobenzene, the reductive elimination of 4,4′-dimethylbiphenyl would most likely occur in a concerted manner involving the coordination and oxidative addition of chlorobenzene.[25] Given that no 4-methylbiphenyl was formed as a cross-coupling product from the *p*-tolyl group in **3** and chlorobenzene, it is likely that any other routes responsible for the separation to monomeric *p*-tolylnickel(I) species from **3** would be negligible during the oxidative addition of chlorobenzene. The reductive elimination of two σ-aryl groups from dinickel centers has also been reported in the literature.[23]

Scheme 6. Stoichiometric Reaction of 3a with Chlorobenzene



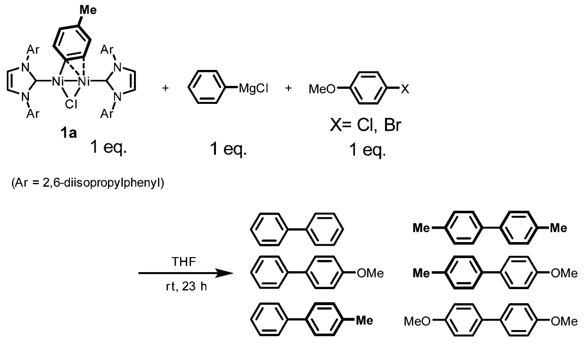
Product Distribution of Biaryls in the Stoichiometric Reactions. Complex **1a** was treated with 1 equiv of 4-chloroanisole in THF for 6 h at room temperature to determine where the bridging σ-aryl group from **1a** ended up in the cross-coupling and/or homocoupling products. It is noteworthy that all of the possible coupling products, including 4,4′-dimethylbiphenyl, 4-methyl-4′-methoxybiphenyl, and 4′4-dimethoxybiphenyl, were unexpectedly detected by GC-MS analysis in this reaction (Scheme 7). The product ratio of these three compounds was 13:37:50. In the catalytic process as given in Table 2, no homocoupling products from aryl halides were detected, showing that the stoichiometric reaction products using **1a** are not consistent with those in the catalytic reactions.

Scheme 7. Stoichiometric Reaction of 1a with *p*-Chloroanisole



Phenylmagnesium chloride was also added to a reaction mixture consisting of **1a** and a stoichiometric amount of 4-chloro- or 4-bromoanisole. After 18 h at room temperature, all of the starting aryl halides had been consumed, and the yields of the extracted biaryl products were determined by GC-MS analysis. All six of the possible biaryl products were detected in this reaction (Scheme 8). Surprisingly, the 4-methoxybiphenyl cross-coupling product was formed in the highest yield (71%) from 4-haloanisole, despite only 1 equiv of 4-haloanisole being added to **1a**. Most notably, the yield of 4-methyl-4′-methoxybiphenyl was much higher than that of 4-methylbiphenyl (e.g., 27 vs 2% from 4-bromoanisole and 9 vs 2% from 4-chloroanisole, respectively) (Figure 3). The former of these two products could also be obtained by the oxidative addition of haloanisole to **1a** (Scheme 7), whereas the latter of the two products could be derived from the reaction of **1a** with phenylmagnesium chloride via the formation of bis(σ-aryl)-dinickel complex **3** (Scheme 6), according to the above stoichiometric reactions. This result therefore confirmed that the oxidative addition process from **1a** to **2** was preferred over the transmetalation process from **1a** to **3**. This result was especially interesting because 4-chloroanisole is usually less active toward the oxidative addition of carbon−chlorine bonds. Reports pertaining to the occurrence of competition between oxidative addition and transmetalation reactions in catalytic cycles are scarce, and the findings presented in the current

Scheme 8. Stoichiometric Reaction of 1a with *p*-Haloanisole and Phenylmagnesium Chloride



Determined by GC-MS

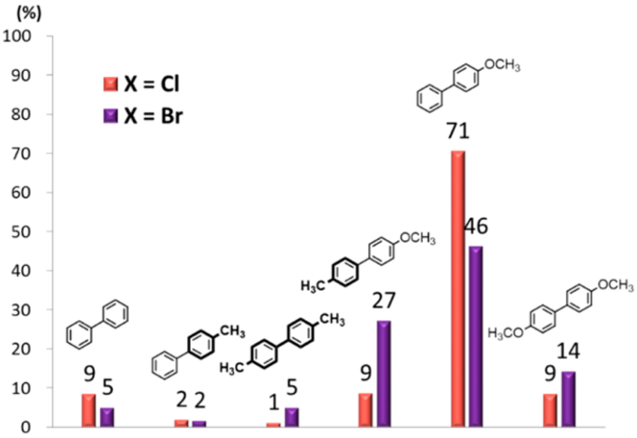


Figure 3. Product distribution of the biaryl derivatives in the stoichiometric reactions of **1a** with MeO(C_6H_4)X (X = Cl, Br) and PhMgCl.

report therefore represent an important development in our understanding of the reactivity of monovalent nickel complexes. Although no supporting results were generated during the course of this study to explain why the rate of the transmetalation reaction was much slower than that of the oxidative addition, it is envisaged that the electron-rich nickel(I) center would disfavor interaction with the electron-rich aromatic carbon of the Grignard reagent. It is also possible that a facile electron transfer process could have occurred from the electron-rich nickel to the aryl halide acceptor.[26]

The product ratios of 4-methyl-4′-methoxybiphenyl and 4-methylbiphenyl were low at 9 and 2%, respectively, in Figure 3, when 4-chloroanisole was used as the substrate. In contrast, the product ratio of 4-methoxybiphenyl generated from 4-chloroanisole was high at 71%. Furthermore, ^{1}H NMR analysis of the crude reaction mixtures showed that the majority of the compound **1a** remained intact after the reactions with 4-chloroanisole, as shown in Figure 4a, whereas compound **1a** was converted almost exclusively to the bromide analogue of compound **2**, [Ni(IPr)]$_2$(μ-Br)$_2$ (**2′**),[13i] when 4-bromoanisole was added to the reaction mixture (Figure 4b). The remarkable contrast in these results indicated that **1a** was in no way involved in the formation of the catalytic product 4-methoxybiphenyl from 4-chloroanisole. It was therefore envisaged that a significant amount of some highly active nickel species was being formed during the course of both of these reactions and that this unknown active species was responsible for the formation of the catalytic product 4-methoxybiphenyl.

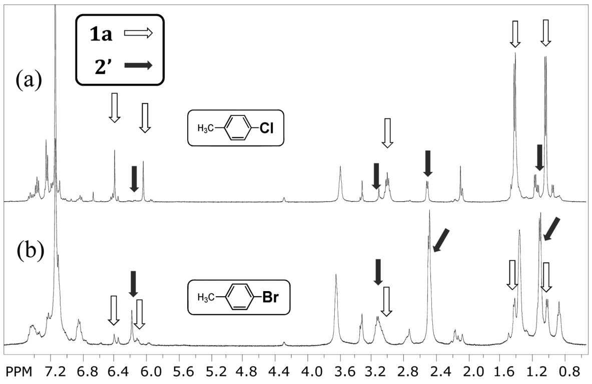
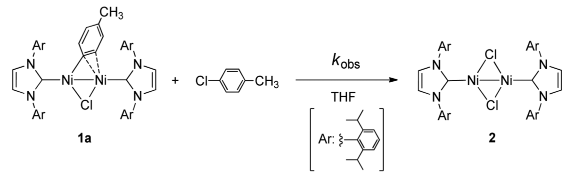


Figure 4. ^{1}H NMR spectra (400 MHz, in C_6D_6, room temperature) of the stoichiometric reaction mixtures using (a) 4-chloroanisole and (b) 4-bromoanisole.

Kinetics and Theoretical Studies in the Oxidative Addition of 4-Chlorotoluene to Dinickel(I) Species 1a. The results of a detailed investigation of the processes involved in the oxidative addition of aryl halides to the dinickel(I) systems, such as **1a** and **2**, could provide significant understanding of how organometallic reactions can proceed on such unsaturated dinuclear systems. It is noteworthy that oxidative addition reactions to monovalent dinickel species are uncommon in comparison with normal zerovalent nickel species. Several different pathways could be proposed to account for formation of **2** and the biaryl products formed during this multistep reaction. For example, a mononickel(III) oxidative adduct could be formed, according to a pathway similar to that proposed in the monomeric nickel(I) system.[6] Alternatively, the addition of an aryl halide species to Ni(I)−Ni(I) could lead to the formation of the dinickel Ni(II)−Ni(II) system (Scheme 1(4)). It was envisaged that the kinetic parameters of the transformation could be estimated by the monitoring of a low-temperature reaction by NMR spectroscopy. Because the reaction proceeds slowly, even at low temperature, it was quite difficult to quench the reaction. After several attempts, the pseudo-first-order reaction rates of **1a** were determined experimentally using a large excess (30 equiv) of 4-chlorotoluene, which could be readily removed under reduced pressure to stop the reaction, at temperatures of −81, −70, −55, and −43 °C. The ^{1}H NMR spectra of the reaction mixture contained an independent signal at δ_H 6.06, which was assigned as the bridging aryl protons in **1a**. This signal rapidly diminished as the reaction proceeded, which indicated that the reaction could be regarded as an irreversible process involving the oxidative addition of 4-chlorotoluene to **1a**, followed by the reductive elimination of 4,4′-dimethylbiphenyl to form **2**. The observed rate constant was defined as k_{obs} (Scheme 9). The concentration of **1a** (C_{1a}) and the time could therefore be plotted according to eq 1.

Scheme 9. Kinetic Parameter k_{obs} in the Stoichiometric Reaction of 1a



$$\ln C_{1a} = -k_{obs}t + \ln C_{1a}^{0} \quad (k_{obs} = kC_{4\text{-chlorotoluene}}) \qquad (1)$$

Four different k_{obs} values were determined depending on the reaction temperatures to give the corresponding Arrhenius plot (Figure 5). The resulting $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G_{298}^{\ddagger}$ values were +2.40 ± 0.12 kcal mol^{-1} (+10.1 ± 0.5 kJ mol^{-1}), −56.52 ± 0.52 cal K^{-1} mol^{-1} (−237.4 ± 2.2 J K^{-1} mol^{-1}), and +19.3 ± 0.3 kcal mol^{-1} (+80.9 ± 1.1 kJ mol^{-1}), respectively. The most striking feature of this reaction was its large negative activation entropy, which was over −50 cal K^{-1} mol^{-1}. The Gibbs free activation energy $\Delta G^{\ddagger}$ was therefore largely dependent on the activation entropy, which suggested that the rate-determining

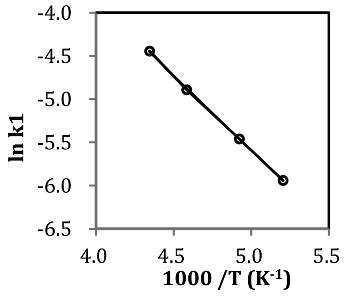


Figure 5. Arrhenius plot of the low-temperature reaction of **1a** with 4-chlorotoluene.

step was more likely to be the coordination of the aryl halide to the nickel species rather than the oxidative addition, reductive elimination, or the reaction responsible for the separation to a monomeric species from the dimeric species (if possible). These results were therefore consistent with the presence of the two bulky NHC ligands around the dinickel centers, which could hinder the approach of an aryl halide molecule, as indicated in Figure 2. However, this suggestion is dependent on the dinickel framework being maintained during the reaction.

$$\ln C_{\mathbf{1a}} = -k_{\mathrm{obs}}t + \ln C_{\mathbf{1a}}^{\ 0} \qquad k_{\mathrm{obs}} = kC_{\text{4-chlorotoluene}} \tag{1}$$

The large negative activation entropy observed for this reaction prompted us to conduct a theoretical investigation of the reaction mechanism using density functional theory (DFT). DFT/PBE0 calculations (free energies in kcal mol^{-1}) based on the use of the complex [Ni(IMe)]$_2$(μ-Cl)(μ:η^1,η^2-C$_6$H$_5$) (**A**) (with the simpler model ligand 1,3-bis(methyl)imidazol-2-ylidene (IMe), instead of IPr) and chlorobenzene (ClBz) as a model substrate provided a conceivable pathway for the reaction (Figures 6 and 7). When a more bulky 1,3-bis(phenyl)imidazol-2-ylidene (IPh) was employed in the DFT calculations, many processes involving subtle rotation movement of the phenyl rings in IPh should be taken into account. However, the overall sequence of the reaction steps using IMe was similar to that with IPh. Therefore, the steric effect of these NHC ligands may not affect the overall sequence so much even when the bulkier NHC ligand is employed for the nickel(I) complexes. Similar dinuclear processes have also been calculated by Schoenebeck et al.[11b−d]

In the initial step, chlorobenzene was added to complex **A** to form intermediate **B**, where the aromatic ring was coordinated to the complex in a η^2 fashion via the carbon atoms at C2 and C3. The location of the transition state **TS$_{AB}$** revealed a moderate activation barrier of 15.5 kcal mol^{-1} (64.8 kJ mol^{-1}). The chlorobenzene group subsequently underwent a ring slippage rearrangement to form **C**, where the aromatic ring was still η^2 coordinated to the complex, but now via the carbon atoms at C1 and C2. During the course of this process, the Ni−Ni bond distance increased from 2.35 Å in **A** to 2.62 Å in **C**, with the concomitant activation of the C−Cl bond. Furthermore, the C−Cl bond distance increased from 1.75 Å in both the free chlorobenzene and **B** to 1.82 Å in **C**. This process was found to be slightly endergonic by 4.7 kcal mol^{-1} (19.7 kJ mol^{-1}) with respect to the initial reactants. During the following oxidative addition step, the C−Cl bond was cleaved and a new Ni−Cl bond was formed to give intermediate **D**, which no longer possessed a Ni−Ni bond (3.30 Å). Furthermore, both of the arene rings in **D** were coordinated to nickel in a σ fashion through a single C atom. The formation of **D** from **C** was found to strongly exergonic, releasing 44.9 kcal mol^{-1} (187.9 kJ mol^{-1}). The Ni−Cl bond started to form

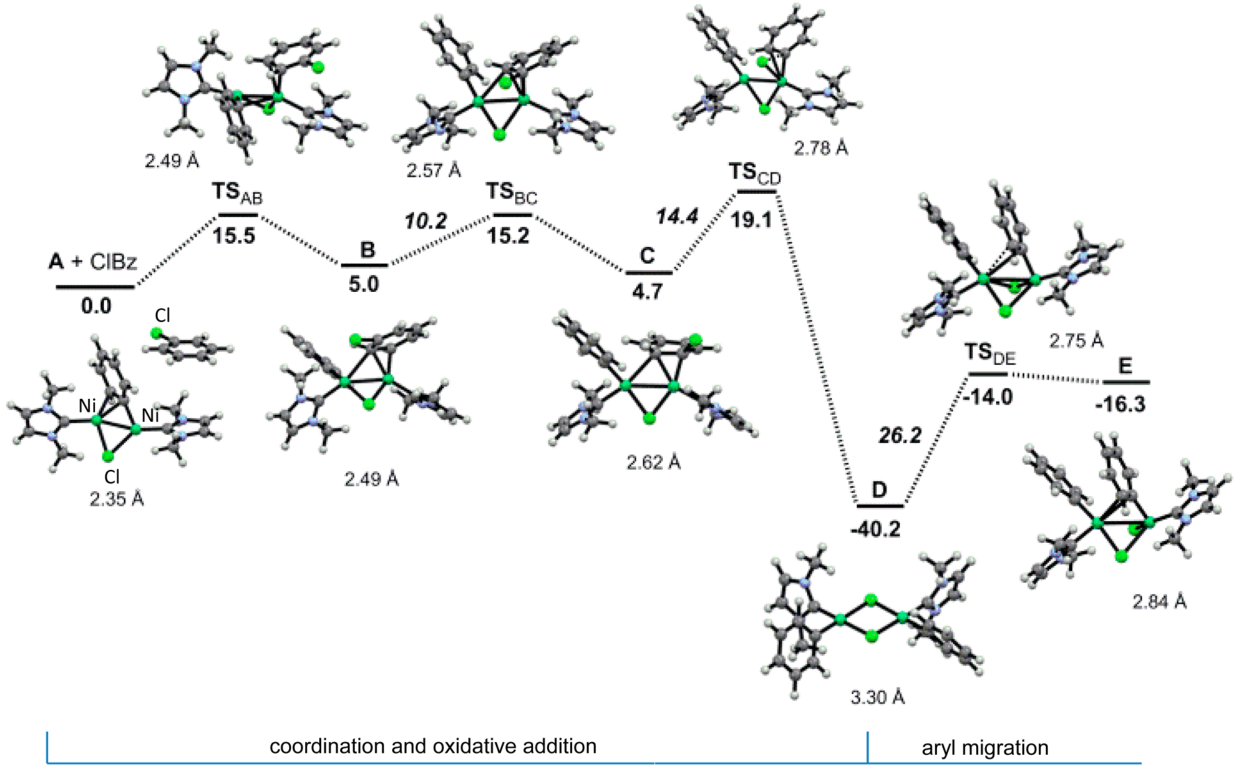


Figure 6. Reaction profile of the computed relative Gibbs free energies (kcal mol^{-1}) for the reaction of [Ni(IMe)]$_2$(μ-Cl)(μ:η^1,η^2-C$_6$H$_5$) (**A**) with chlorobenzene (ClBz) to give intermediate **E** (Ni−Ni bond distances in Å).

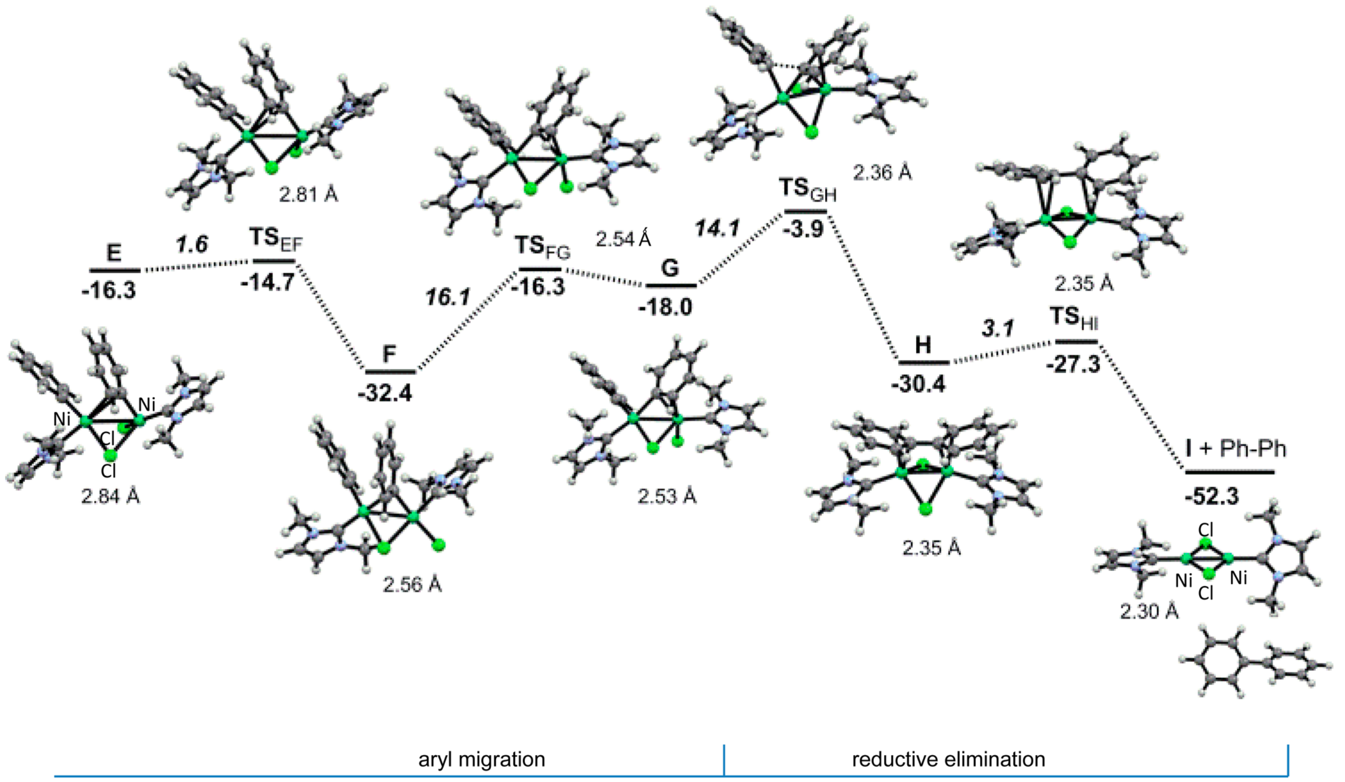


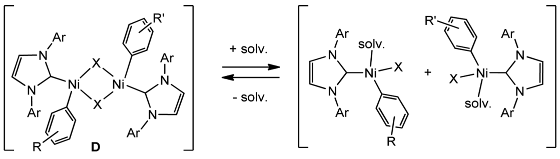
Figure 7. Reaction profile of the computed relative Gibbs free energies (kcal mol^{-1}) for the reaction of intermediate **E** to give the final products $[Ni(IMe)]_2(\mu\text{-}Cl)_2$ (**I**) and biphenyl (Ni−Ni bond distances in Å).

during this step, going from 3.12 Å in **C** to 2.76 Å in **TS$_{CD}$** and ultimately reaching 2.25 Å in **D**. This step was accompanied by the concomitant cleavage of the C−Cl bond, with the C···Cl distance increasing from 1.82 Å in **C** to 2.35 Å in **TS$_{CD}$** and finally becoming 3.00 Å in **D**.

In the following step, one of the two η^1-bound aryl ligands was brought into a bridging position ($\mu\text{-}\eta^1,\eta^2\text{-}C_6H_5$) to give intermediate **E** via **TS$_{DE}$**. The bridging aryl moiety in intermediate **E** was η^2-coordinated to a Ni center containing a σ-coordinated aryl ring. This process required free activation energy of 26.2 kcal mol^{-1} (109.6 kJ mol^{-1}) from **D** and was endergonic by 23.9 kcal mol^{-1} (100.0 kJ mol^{-1}), but the free energy of the transition state **TS$_{DE}$** was still 14.0 kcal mol^{-1} (58.8 kJ mol^{-1}) lower than that of **A** + ClBz. The Ni−Ni distance was reduced to 2.84 Å following this step. During the following two steps (i.e., **E** → **F** and then **F** → **G**), there was a reorientation of the $\mu\text{-}\eta^1,\eta^2\text{-}C_6H_5$-bound aryl ligand, which brought the aryl moieties together to enable the formation of the C−C bond of the biphenyl product (note that the C−C bond distance in **E** was 3.13 Å). In **F**, the C−C bond distance was reduced to 2.73 Å, and the aryl ligand was coordinated in a $\mu\text{-}\eta^1$ fashion. However, in **G**, the aryl unit was once again bound to the Ni in a $\mu\text{-}\eta^1,\eta^2$ mode but was now also η^2 coordinated to the other Ni center bearing no σ-aryl ring. Finally, the formation of the C−C bond of the biphenyl product occurred via **TS$_{GH}$** (d_{C-C} = 1.96 Å) to give complex **H** (d_{C-C} = 1.48 Å), where the newly formed biphenyl (Ph-Ph) molecule was coordinated in a $\mu\text{-}\eta^2,\eta^2$ fashion. This process was determined to be facile, with a free energy barrier of only 14.1 kcal/mol using IMe as the model spectator ligand. In the final step the Ph-Ph ligand was released to give the complex $[Ni(IMe)]_2(\mu\text{-}Cl)_2$ (**I**) in an exergonic reaction (ΔG = −21.9 kcal mol^{-1} (−91.6 kJ mol^{-1})). The overall reaction from **A** to **I** was found to be exergonic by −52.3 kcal mol^{-1} (−218.8 kJ mol^{-1}).

Remarkably, the relative Gibbs free energy of the most stable intermediate **D**, −40.2 kcal mol^{-1} (−168.2 kJ mol^{-1}), was still 12 kcal mol^{-1} (50.2 kJ mol^{-1}) higher than that of the final products, $[Ni(IMe)]_2(\mu\text{-}Cl)_2$ (**I**) and the biaryl compound. The result suggested that the compound **D** is the metastable intermediate over the oxidative addition and reductive elimination processes. The structure of **D** revealed that the terminal σ-aryl moiety located at the position adjacent to that of the carbene ligand could cause steric repulsion between the carbene and the σ-aryl moiety. Given that there was no bonding interaction between the nickel atoms in **D**, the equilibrium for the cleavage of the Ni−Cl bond by disproportionation could ultimately lead to the formation of the mixed biaryl products (Scheme 10).

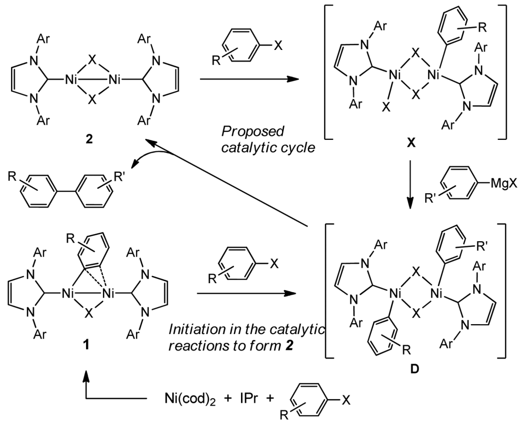
Scheme 10. Possible Disproportionation Equilibrium



The initial coordination of the chlorobenzene substrate to the nickel atom had the largest activation barrier of all of the steps in the process, and its activation entropy was estimated to be −70 J K^{-1} mol^{-1}. The theoretical pathway in Figure 6 could be consistent with the real pathway, because the rate-limiting process would be the coordination of the aryl halide also in calculations. As indicated by the kinetics, the more sterically hindered IPr ligand would most likely require considerable negative activation entropy. Furthermore, the coordination of the aryl halide would most probably require activation energy higher than that calculated using IMe. In any case, the most important feature of this calculation is that the whole process is conducted on dinickel centers, which supports our hypothesis that this catalytic cycle involves both [Ni(I)−Ni(I)] and [Ni(II)−Ni(II)] species.

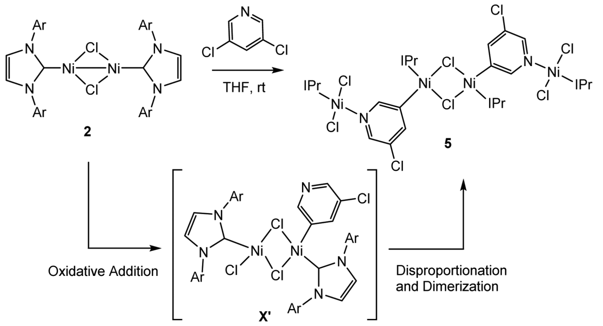
Alternative Catalytic Cycle Involving 2. In the stoichiometric reaction of **1a** with both 4-chlorotoluene and phenylmagnesium chloride, the consumption of **1a** was much slower than that of 4-chlorotoluene, which was consumed to form the product in catalysis (Figure 4). Furthermore, the distribution of the mixed biaryl products in the stoichiometric reaction of **1a** or **3** was completely different from that observed after the catalytic Kumada cross-coupling reaction, yielding only one cross-coupling product, where the stoichiometric reactions afforded all of the possible biaryl products as a result of a disproportionation reaction (Scheme 10). These experiments revealed that the catalytic cycles proposed above between **1a** and **2** and between **1a** and **3** are not involved in the real catalytic cycle. On the other hand, these results strongly support the following alternative pathway as shown in Scheme 11. Oxidative addition of aryl halide to complex **2** would lead to the formation of a dinickel(II) adduct (**X**), and subsequent transmetalation with a Grignard reagent would give a nickel(II) diaryl species (**D**), which would undergo a facile reductive elimination reaction to give the biaryl product with the concomitant regeneration of complex **2**. This alternative cycle was believed to be much more likely than any of the other cycles for the following reasons. In comparison with complex **1a**, complex **2** seems to be sterically less hindered, and the reactions with aryl halide on **2** to give the intermediate **X** may not require such a large negative entropy, which was observed in the kinetic study of **1a** with 4-chlorotoluene. Therefore, this process would occur with greater ease than the corresponding reaction onto the more hindered compound **1a**. These reactions including oxidative addition and reductive elimination with the complex **2** in Scheme 11 are regarded as the processes similar to the calculated ones, which are shown in Figure 6. Additionally, a theoretical study of the process from **2** to **X** was also conducted using DFT calculations with the 3-21G basis set for C, H, and N, 6-31G* for Cl, and CEP/LanL2DZ for Ni. The results of this study led to the proposal of a similar dinickel activation pathway, including the coordination and oxidative addition of chlorobenzene to dinickel(I) dichloride (see the Supporting Information). The initiation process from the mixture of Ni(cod)$_2$, IPr, and aryl halide easily affords **1** and then **2** (Scheme 11), as the result of the reaction of **1** with aryl halide, indicating that this alternative cycle is also readily accessible from the general in situ catalyst system using nickel precursor and IPr.

Scheme 11. Alternative Possible Catalytic Cycle Mediated by 2 and the Initiation Process Involving the Catalysis Reaction of 1 with Aryl Halide



Although we cannot determine the intermediary compound **X** from the reaction of **2** with aryl halides, we obtained a oxidative addition product from the stoichiometric reaction of **2** with 3,5-dichloropyridine at room temperature (Scheme 12). A single crystal suitable for X-ray crystallography was obtained following the concentration of a reaction mixture of **2** with 3,5-dichloropyridine. The divalent tetranickel complex **5** was successfully determined by X-ray diffraction analysis (see the Supporting Information). That is, oxidative addition of aryl chloride on **2** can occur, suggesting the possibility of formation of the intermediate **X** in the catalytic cycle from **2** and aryl halide.

Scheme 12. Oxidative Addition Product 5 from 2 and 3,5-Dichloropyridine and Proposed Intermediate X′ in the Reaction



The most important point found in these mechanistic studies is that the oxidation and reduction processes in these dinickel(I) complexes are most likely distinct from the corresponding mononuclear Ni(I) and Ni(III) redox processes. Ni(III) complexes are generally synthesized by electrochemical oxidation or the oxidation of Ni(II) complexes with dioxygen.[27] In contrast, the oxidation states of the two nickel(I) centers increased from +1 to +2 in the current study during the oxidative addition of the aryl halide (Scheme 1). The bridging halogen ligand could play an important role in maintaining the proximal positions of both the nickel centers. Furthermore, the bulky NHC ligand IPr kinetically stabilized the dinuclear nickel(I) framework in a way that cannot be obtained for the smaller IMes ligand. Dinuclear systems of this type are consistent with the large negative entropy ($\Delta S^{\ddagger} = -56.52 \pm 0.52$ cal K^{-1} mol^{-1}) observed in the reaction of the similar dinickel(I) system **1a** with aryl halide followed by the reductive elimination of the corresponding biaryl product.

■ CONCLUSIONS

Intermediary monovalent dinickel complexes have been found using a nickel(0) catalyst precursor and a bulky N-heterocyclic carbene ligand in the Kumada−Tamao−Corriu cross-coupling reaction of aryl halides. The compounds were obtained by oxidative addition of aryl halides to a Ni(0) precursor and were coordinatively unsaturated (30e), dinuclear *μ*-*σ*-aryl-*μ*-chloro nickel(I) species, which could react with both aryl halides and Grignard reagents. Further reaction with aryl halides yielded the C(Ar)−C(Ar) bond coupled biaryl products together with a (μ-chloro)nickel(I) dimer, whereas transmetalation with a Grignard reagent afforded bis(μ-σ-aryl)dinickel(I) complexes.

Both of these dinuclear complexes had the same dinickel(I) framework as the complex **2** and can be regarded as at least the analogues of the real active species in the catalytic cycle. Therefore, stoichiometric reactions of these complexes concerning the catalytic reaction were investigated. Experiments showing faster oxidative addition in comparison to transmetalation on the dinickel(I) complexes indicated the possible reaction order of these complexes in the presence of both aryl halide and Grignard reagent. Kinetics for the oxidative addition of an aryl halide and the subsequent reductive elimination of a biaryl product showed large negative entropy, which suggested that the coordination of the aryl halide could be the rate-determining step as a consequence of the steric hindrance derived from the two bulky NHC ligands.

Although the semistable dinickel(II) intermediate, which would be formed by the reaction of the dinuclear μ-σ-aryl μ-chloro nickel(I) species with aryl halide, cannot be uncovered in this study, theoretical studies strongly suggested that coordination and oxidative addition of aryl halide onto the unsaturated nickel(I) species led to formation of the nickel(II) intermediate, retaining its dinuclear framework. It was of interest that the Gibbs energy of the divalent intermediate was still higher than that of the final (μ-chloro)nickel(I) dimer, making it possible to smoothly restart the catalysis. However, this cycle was negligible in the real catalytic system, as concluded from the experimental results.

On the other hand, the above results were very helpful in understanding the most possible catalytic cycle via the formation of the dinickel(I) μ-chloride complex **2** as the key compound in the catalytic process. It would allow for the faster oxidative addition of an aryl halide to form the divalent dinickel species, in comparison with the reaction with the starting dinuclear μ-σ-aryl μ-chloro nickel(I) complex **1**, because of possessing the less-hindered nickel centers in **2**, which would be immediately regenerated by transmetalation of the divalent dinickel species with a Grignard reagent and subsequent reductive elimination to give the cross-coupling products, enabling a fast catalytic process. It was quite interesting that the dinuclear system in oxidative addition of aryl halide and reductive elimination of biaryl works efficiently in the cross-coupling reaction. The DFT calculations for the mechanism revealed that oxidative addition occurs on one of the unsaturated nickel centers and then one of the terminal aryl groups migrates to the bridging position to couple with the aryl group on the other nickel. Moreover, the biaryl just after the C−C bond formation coordinates to both nickel centers. Such cooperative processes make the catalytic cross-coupling occur smoothly without a large energy barrier, led by the dinuclear system. We are conducting studies to apply the catalyst system to other cross-coupling reactions, these being generally challenging processes for nickel catalysts.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00451.

Experimental details, DFT calculation details, crystal structures of **1b** and **4** (PDF)

Full crystallographic descriptions (CIF)

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Notes

The authors declare no competing financial interest.

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